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# **An Enhanced Gas Ionization Sensor from Y-doped Vertically Aligned Conductive ZnO Nanorods**

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## **Abstract**

A stable and highly sensitive gas ionization sensor (GIS) constructed from vertically aligned, conductive yttrium-doped ZnO nanorod (YZO NR) arrays is demonstrated. The conductive YZO NRs are synthesized using a facile one-pot hydrothermal method. At higher Y/Zn molar ratio, the aspect ratio of the YZO NRs is increased from 11 to 25. Doping with yttrium atoms decreases the electrical resistivity of ZnO NRs more than 100 fold. GIS measurements reveal a 6-fold enhancement in the sensitivity accompanied with a significant reduction in breakdown voltage from the highly conductive YZO NRs. Direct correlations between the resistivity of the NRs and GIS characteristics are established.

**Keywords:** Gas ionization sensor; Conductive ZnO nanorod; Hydrothermal synthesis

## **1. Introduction**

Chemical sensors have attracted considerable attention in recent years because of the need to optimize the sensitivity and selectivity of industrial automatic feedback controls used in pollution detection; environmental monitoring; and biomedical and pharmaceutical applications [1-3]. Gas sensors are generally classified as chemical or physical types based on their operational mechanism. Most of the conventional gas sensors are of the chemical type in which chemisorbed target gases on metal oxide [4-7], silicon [8] and carbon nanotube (CNT) [2, 9, 10] substrates are quantified by the responses of their electrical [11] or optical property [12]. However, these types of sensors suffer from limited selectivity [11, 13] and difficulties in detecting gases with poor adsorption. Normally, a high working temperature is required to establish adsorption/desorption equilibrium [1].

With the capability of qualitative and quantitative measurements of gases at room temperature, gas ionization sensors (GISs) offer distinctive selectivity with high sensitivity

for many gases. As a physical type of gas sensor, it measures the ionization energy [14] and the discharge current of gases [15]. The characteristic ionization energies of gas molecules are used to identify gases, while the amplitude of the ionization current is proportional to the logarithm of the partial pressure of the gas components [15, 16]. GISs are ideally used in advanced gas analyzers for chromatography and mass spectrometry or for specific industrial environment [17]. Meanwhile, a GIS could also be used as a non-radioactive, ionization source which could be coupled with mass spectrometers, such as ion mobility spectrometry (IMS) [18]. A stable GIS operated at room temperature with low power consumption could improve the performance and versatility of IMS. Although, in comparison with the surface thermal ionization gas sensors [19-22], the dynamic range of GISs are restricted by gas discharge behaviour, their sensitivity can be controlled by adjusting the discharge field strength.

Important criteria for high quality GIS sensors are high sensitivity, good stability and large dynamic range. Industrial applications of gas sensors require high stability, which lower the maintenance cost and improve their detection reliability, while large dynamic range offers versatility of the application environment, such as in combustion engine exhaust gas monitoring. On the other hand, high sensitivity could substantially reduce the lower limit of detection. For GISs, higher sensitivity corresponds to a higher discharge current, and stability is related to the stability of the discharge voltage.

The aim of this paper is to develop nanomaterials that are suitable for GIS application with high reliability; good electrical and chemical stability; and high sensitivity. GISs based on conductive vertically aligned 1D nanomaterials, such as CNTs and metallic nanowires, have been demonstrated with high sensitivity [23, 24]. However, their performance can be rapidly deteriorated, suffering from degradation by residual gases like O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and CO. Metal oxides are normally stable under such oxidative environments. GISs with good

stability have been achieved with 1D metal oxide nanostructures, including ZnO nanorods (NR) [17], CuO NRs [14] and TiO<sub>2</sub> nanotubes [25]. However, much higher breakdown voltages were required due to lower electrical conductivity, resulting lower discharge current and detection sensitivity.

Our strategy is to develop high aspect ratio, conductive metal oxide NRs with the synergetic advantages of chemical stability, optimized morphology and improved electrical properties. Conductive metal oxides, such as ZnO, can be achieved by doping with metals such as Na, Al and Y [26-31]. Such highly conductive metal oxides have been widely used in optoelectronic applications [32-35]. In the field of gas sensors, the application of conductive ZnO NRs is limited to chemical sensors [36-39], while currently there is no reported application in the field of GISs.

Here, for the first time, we demonstrate a stable GIS using vertically aligned conductive YZO NR arrays (Fig. 1). We report on a facile one-pot hydrothermal method to synthesize the high quality crystallized YZO NR arrays with optimized conductivity for high GIS sensitivity. The effects of doping on the morphology of the ZnO NRs are systematically studied. The correlation between physical properties and the dopant concentrations in the ZnO is also investigated. Under optimized doping condition, the sensitivity of the YZO NR GIS is improved by a factor of 6, while the breakdown voltages for the tested gases are reduced by 85 V on average.

## **2. Experimental Section**

### **2.1 Synthesis and Method**

All chemicals used were analytical grade and purchased from Sigma-Aldrich UK. Polished high purity copper plates (2 mm thickness, 1 × 1.5 cm<sup>2</sup>) were used as substrates, which were cleaned under sonication in an isopropanol bath for 15 minutes and rinsed thoroughly with deionized (DI) water, followed by drying in air.

A hydrothermal synthesis method was used to grow ZnO NRs on copper substrates. The synthesis involves two main steps: seeding and growth. The seeding solution was prepared by dissolving 0.219 g zinc acetate in 10.0 mL DI water. The substrates were spin coated (speed  $\approx$  300 rpm, time  $\approx$  30 s) with the seeding solution followed by annealing at 250°C for 20 minutes in order to convert the zinc acetate into ZnO seeds. The reaction solution was prepared by dissolving 0.136 g of zinc chloride in 10 mL of DI water. For YZO nanostructures, different concentrations of yttrium nitrate hexahydrate with Y/Zn molar ratio percentages of 0.5, 1.0, 2.0 and 3.0 were added to the growth solution. Ammonia solution (25%, 0.5 ml) was added dropwise into the growth solution (10 mL) to increase the solution pH to 10.0. Then 8 mL of the growth nutrient solution was added into a 10 mL Teflon vessel with a seeded copper plate immersed into the reaction solution. The sealed hydrothermal vessel was heated in an oven at 95°C for 120 minutes. Subsequently, the vessel was cooled down to room temperature. The as-grown sample was rinsed with DI water three times and dried at room temperature.

## **2.2 Structural and Physical Characterization**

The surface morphologies of the samples were studied by scanning electron microscopy (SEM, JSM 820M, Jeol). The crystallinity and structure orientation of the nanostructures were analyzed by powder x-ray diffractometer (XRD, Siemens D500). The average diameters and film thicknesses were measured from top- and side-view SEM images using Image J software (National Institutes of Health, USA). The light absorption spectra were recorded using a UV-Vis spectrophotometer (Thermospectronic UV 300) with samples grown on fluorinated tin oxide glass substrates (FTO, supplied by Sigma-Aldrich UK) under identical conditions. The actual Y concentrations in the ZnO NRs were measured using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce). The electrical

resistance of the samples was measured using a four-point probe with pin diameter of 1.80 mm and an interval of 3.40 mm between the adjacent pins.

### **2.3 Gas Ionization Sensor Testing**

The GIS consists of two electrodes where a ZnO NRs plate was used as the anode and an FTO glass as the cathode electrode, separated by a polytetrafluoroethylene (PTFE) spacer with the gap distance adjusted in the range from 30 to 200  $\mu\text{m}$ . The active areas of the GIS devices were fixed at 1  $\text{cm}^2$ . The device was loaded into a stainless steel gas chamber with glass windows. The test chamber was evacuated before the desired gas was introduced through a leak valve. The gas pressure was monitored using a digital Pirani gauge (KJLC, 317 series). The applied DC voltage can be continuously adjusted from 0 V to 3 kV (Pharmacia, ECPS 3000/150) and the discharge current is recorded using a digital multimeter.

## **3. Results and Discussion**

### **3.1 Morphology and Structure Characterization**

The morphology of the NR nanostructure can be significantly affected by the growth environment and conditions, depending on the surface adsorption and passivation. For GIS applications, smaller diameters of NRs have the advantages of lower discharge voltage, since the electrical potential is relatively focused. The morphologies of the YZO NRs as a function of Y dopant concentrations were studied by SEM, shown in Fig. 2. It reveals that doping of Y ions did not affect the growth orientation of ZnO NRs. However, as the Y/Zn molar percentage increases, the average diameter of the NRs decreases monotonically, shown in Fig. 2F. The actual Y concentrations in the ZnO NRs were determined by ICP-MS, giving molar percentages of 0.05 at% ( $\text{Y}_{0.05}\text{ZO}$ ), 0.10 at% ( $\text{Y}_{0.10}\text{ZO}$ ), 0.13 at% ( $\text{Y}_{0.13}\text{ZO}$ ) and 0.17 at% ( $\text{Y}_{0.17}\text{ZO}$ ), respectively (Table S1, Supplementary Material).

The reduction of the diameters is also accompanied by an increase of the NR lengths as shown in the side view SEM images in Fig. S1A-E, summarized in Fig. S1F,

Supplementary Material. Such morphology changes imply that the presence of  $Y^{3+}$  or  $NO_3^-$  suppresses the growth of ZnO along the NR sidewall, leading to narrower and longer NRs. Previous dip coating experiments showed similar effects using  $YCl_3$  [40], hence negatively charged  $Y^{3+}$  complexes are likely responsible for the shape of the YZO NRs by bonding to the positively charged ZnO (100) plane [41]. Similar behavior has been reported for other  $X^{3+}$  ions, including  $Al^{3+}$ ,  $Ga^{3+}$  and  $In^{3+}$  [41]. The measured aspect ratio for the YZO NRs is plotted in Fig. 3. It is clear that as the Y concentration increases, the aspect ratio of the NRs increases monotonically from 10.8 (0 at%) to 25.1 (0.17 at%). Meanwhile, the density of the YZO NRs is also increased, as observed from SEM images in Fig. 2A-E.

The crystallinity of as-grown ZnO and YZO NRs on copper substrates was analyzed by powder diffraction in comparison with the standard XRD database for hexagonal phase wurtzite ZnO (JCPDS 36-1451) in addition to copper substrate signal (JCPDS 04-0836). In all the samples, as shown in Fig. 4, the diffraction from (002) planes is dominant, typical for the vertical alignment of the NRs with (002) plane parallel to the substrate. Since there was no diffraction from yttrium oxide phases observed, the  $Y^{3+}$  concentrations could be too low and the Y ions were homogeneously distributed in the ZnO crystals. An increased intensity of the main ZnO peak can also be observed with increasing  $Y^{3+}$  doping concentration. This phenomenon further confirms that  $Y^{3+}$  suppresses the growth of ZnO along the NR sidewall, and promotes the growth of ZnO on (0001) direction.

On the other hand, the (002) diffraction peaks were systematically shifted towards smaller angles while their width increased slightly as the Y doping was increased. Thus, the associated ZnO lattice parameters and the unit cell size were increased (Fig. S2, Supplementary Material) [42]. Naturally, both substitutional and interstitial Y dopants were present in the one-pot hydrothermal synthesized ZnO NRs. However, it is the substitutional  $Y^{3+}$  ions responsible for the expansion of the crystal lattice constant due to the larger ionic



radius of  $Y^{3+}$  (0.92 Å) with respect to  $Zn^{2+}$  (0.74 Å) [43], an observation consistent with the literature [40, 44]. Additional evidence for the substitutional  $Y^{3+}$  responsible for the expansion of the ZnO lattice constant was demonstrated from the gradual shifting of electron binding energy of  $Zn^{2+}$  and  $O^{2-}$  as a function of Y doping concentrations [45]. Meanwhile, the width of the (002) diffraction peak increases slightly as the Y dopant concentration increases, indicating the reduction of crystal domain sizes and the deterioration of the ZnO crystallinity. For instance, the crystal domain sizes were decreased from 28.4 nm (ZnO) to 22.7 nm ( $Y_{0.17}ZnO$ ) (Fig. S2, Supplementary Material).

### 3.2 Optical and Electrical Properties

The presence of substitutional  $Y^{3+}$  ions requires the incorporation of nearby  $Zn^{2+}$  vacancies, which act as donors with their energy level positioned close to the conduction band of ZnO. This extra donor state can directly reduce the band gap energy of ZnO. Our UV-Vis absorption study confirms the systematic decrease of band gap energies as the Y doping concentration increases, shown in Fig. S3 in the Supplementary Material.

More important, the electrical resistivity of ZnO can be reduced by Y doping. This electrical behavior could improve the performance of GIS, since the electrical potential gradient along the longer axis of the metal oxide NRs is minimized, achieving a higher electrical field on the apex of the vertically aligned NRs.

Fig. 5 displays the electrical resistivity of ZnO and YZO NRs with various Y concentrations. Since the outer diameter of the four-point probe (1.80 mm) is much larger than the average diameter of the as-grown ZnO NRs (<160 nm), the NR arrays could be considered as a continuous thin film. With increasing Y concentration, the average electrical resistivity of the samples was first decreased rapidly followed by an increase as the Y concentration rose above 0.10 at% (Fig. 4). A minimum electrical resistivity of 0.84  $\Omega \cdot cm$  was obtained, corresponding to a 115 times reduction with respect to the pristine ZnO NRs.

Further increase in the Y concentration increased the resistivity, which suggests that not all the Y atoms in the ZnO film are acting as substitutional dopants. Higher doping levels will increase the interstitial dopant concentration. The interstitial Y atoms will segregate at the crystal domain boundaries, reduce the crystal domain size and increase the structural disorder, which was confirmed by the XRD measurement. More importantly, the interstitial Y atoms are electrically inactive or even act as ‘electron traps’, which effectively passivate existing donors [40]. Thus the resistivity will increase with Y dopant concentration above a certain threshold (0.10 at%), accompanied by the reduction of crystal domain size. Similar observations were reported for Al and Ga doped ZnO [46, 47].

### **3.3 GIS Performances**

Both the sharp needle-like morphology and the reduced resistivity of the NRs could help to improve the performance of the GIS. During the ionisation measurement, by increasing the applied voltage, the discharge current will remain zero until the discharge voltage is achieved. Then a discharge current will be observed. This current will remain as constant, even if the voltage is increased above the discharge voltage. The benchmark GISs were constructed with pristine ZnO NRs as an active electrode. Its performance was tested in air (Fig. S4A, Supplementary Material), with an electrode gap of 80  $\mu\text{m}$ . ZnO NRs based GIS operates at lower breakdown voltage (470 V) with higher discharge currents (29.4  $\mu\text{A}$ ) in comparison to GIS with two parallel copper plates (740 V and 6.1  $\mu\text{A}$ ). This result shows that NR morphologies can significantly improve the performance of the GIS. The breakdown voltage is primarily determined by the gas ionization characteristics [17] and is less affected by the gas pressure (Fig. S4B, Supplementary Material). However, it can be significantly reduced by decreasing the gap distance (Fig. S4C, Supplementary Material), which affects the electrical field strength at the apex of NRs and improves the acceleration of free electrons.

When the gap distance is smaller than 30  $\mu\text{m}$ , the device becomes unstable, therefore all the YZO NR GISs reported in this work have their gap distances fixed at 80  $\mu\text{m}$ .

While the breakdown voltage is used to identify the gas species, the discharge current can be used to quantify the gas. Our measurements show that the discharge current is proportional to the logarithm of gas pressure (Fig. S4D, Supplementary Material) and covers several orders of magnitude from 1 to  $10^3$  mbar and beyond. This gives the GIS advantage of a large dynamic range as a quantitative chemical sensor.

The time response of our sensor was tested from the  $\text{Y}_{0.10}\text{ZO}$  NRs GIS in air at different gas pressure, shown in Fig. S5, Supplementary Material. However, the observed time response was dominated by the filling and evacuating speed of our gas chamber rather than the true response time of the sensor. In fact, the theoretical simulation suggested that the ionisation process had the breakdown time scale of several nano seconds [48].

The performance of the YZO NRs GISs was systematically tested in different gas environments, including air,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and Ar, at a fixed standard atmospheric gas pressure (1000 mbar). Fig. 6 presents the  $I$ - $V$  curves for the electrical breakdown of gas species in the YZO NRs based GISs. The quantitative details of the GIS responses to different gases are summarized in Table S2 (Supplementary Material). It is noticed that each gas exhibits a distinct breakdown voltage. With pristine ZnO NRs, the breakdown voltages were found to be 550, 529, 511, 470, 450, and 282 V for  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CH}_4$ , air,  $\text{N}_2$  and Ar, respectively. Such sequence of the breakdown voltages for different gases is consistent with the literature [49]. The difference in breakdown voltages provides a “fingerprint” for gas identification. For YZO NRs based GISs, the breakdown voltages for all the target gas species were initially decreased as the Y concentration increases until they reach their minimum at 0.10 at% of Y. The opposite trend could be found for the discharge currents. Specifically, the breakdown voltages from the  $\text{Y}_{0.10}\text{ZO}$  NRs GIS are 418, 430, 372, 410, 422

and 230 V for air, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and Ar, respectively. This result represents an averaged reduction of breakdown voltages by 85 V.

The ionization process follows Townsend's mechanism and the breakdown voltage,  $V_{bd}$ , is determined by the Paschen's law given by Eq. (1), where  $p$  is the gas pressure,  $d$  is the gap space between the electrodes, and  $\gamma$  is the secondary Townsend coefficient [50].

$$V_{bd} = \frac{Bpd}{\ln(Apd) - \ln[\ln(1 + 1/\gamma)]} \quad (1)$$

The constants  $A$  and  $B$  are specific for each gas and both are proportional to the ion scattering cross-section. Thus, they are proportional to the square of ion radius. In addition,  $B$  is also proportional to the gas ionization energy [51]. Therefore, the  $V_{bd}$  is determined by the ionization energy as well as the ion radius. For a GIS with smaller gap between electrodes, the  $V_{bd}$  is less sensitive to the gas pressure, then the  $V_{bd}$  becomes unique for a specific gas molecule. The secondary Townsend coefficient,  $\gamma$ , represents the net number of secondary electrons (Auger electrons) produced by a cation scattering on the cathode. For the cathode material with lower work function, the  $\gamma$  value will be higher [51], which results in a lower  $V_{bd}$  from Eq. (1). In our research, the Y<sup>3+</sup> doping in ZnO reduces the electrical resistivity and the work functions of the NRs. This explains the observed significant reduction of the  $V_{bd}$  under optimal doping condition.

The sensitivity of the GIS sensors can be specified by  $\Delta I/\Delta(\log P)$ . The measured sensitivities of GISs with different Y dopant concentration for different gases are listed in Table 1. It is clear that the Y<sub>0.10</sub>ZnO NRs GIS have the highest sensitivity among the GISs at different Y concentrations. Meanwhile, although N<sub>2</sub> has the medium ionization voltage, it has the highest sensitivity among our tested gases. The literature values from GISs based on ZnO NRs [17], CNTs [15], and Pd capped ZnO NRs [52] are also listed for comparison.

It is noteworthy that discharge currents generated from all YZO NRs based GISs are much higher than those of the ZnO NRs based GIS for all tested gases, indicating higher

sensitivity. The GIS based on pure ZnO NRS gives the lowest sensitivity for all gases, which is consistent from the literature [17]. However, by adding Pd clusters [17] or using CNTs [15], the sensitivity can be increased significantly. The highest discharge currents were achieved from the Y<sub>0.10</sub>ZO NRs based GIS. In particular, for O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> gases, the discharge currents were 89.8, 203.9 and 118.3  $\mu$ A on Y<sub>0.10</sub>ZO NRs based GIS, increased from 15.1, 32.0 and 18.1  $\mu$ A on pristine ZnO GIS, respectively. Therefore, the Y<sub>0.10</sub>ZO NRs based GIS exhibits a sensitivity enhancement as high as 6.0~6.5-fold with respect to ZnO NRs based GIS. However, by further increasing the Y concentration, although the diameter of the YZO NRs was further decreased, the breakdown voltages were increased and the discharge currents were decreased.

The discharge current density,  $J$ , from the NR tips can be calculated according to the modified Fowler-Nordheim (FN) equation given by [53]:

$$J = \frac{CE_{tip}^2}{\phi} \exp\left(-\frac{D\phi^{3/2}}{E_{tip}}\right) \quad (2)$$

where  $C$  and  $D$  are the universal FN constants,  $\phi$  is the work function of the NRs cathode. Since Y<sup>3+</sup> doped ZnO NRs have smaller  $\phi$ , Eq. (2) gives higher discharge current density,  $J$ .  $E_{tip}$  is the effective electrical field on the tip of the NRs, given by [48]:

$$E_{tip} = 0.7 \frac{LV}{rd} \quad (3)$$

where  $V$  is the voltage applied between electrodes and the  $d$  is the separation between the electrodes. The strength of  $E_{tip}$  is, however, also significantly affected by the aspect ratio of the NRs determined by the ratio of their length to the radius. For longer and sharper YZO NRs, the aspect ratio is higher and so is the  $E_{tip}$ , resulting in higher discharge current from Eq. (2) and therefore, higher sensitivity of the GISs.

The stability of Y<sub>0.10</sub>ZO NRs based GIS was also tested in air and N<sub>2</sub> environments. Fig. 7A shows the breakdown voltages recorded continuously in 100 cycles at 1000 mbar gas

pressure with a duration of 2 minutes for each cycle. It is noted that the breakdown voltage fluctuates less than 5%. The morphology of the  $Y_{0.10}ZnO$  NRs after 100 cycles of continuous breakdown in  $N_2$  environment was characterized by SEM. There appears to be no significant change in the NR morphology after 100 test cycles (Fig. 7B and C). Such excellent stability is determined by the inertness of the metal oxide materials in a reactive environment, which is essential for the reliability of the GIS.

### **3.4 Mechanism of GIS sensitivity enhancement**

Potentially, both the average diameter and the resistivity of the YZO NRs could affect the breakdown voltages and discharge currents. The decrease in the diameter and increase in the aspect ratio of the YZO NRs could help to achieve a more focused electrical field at the apex of the NRs, achieving a large field enhancement in the field emission process. However, our experimental data do not always show a monotonic negative correlation between the discharge currents and the diameters of the NRs. For instance, when the Y concentration was above 0.1 at%, the reduction of NR diameter does not increase the discharge currents. Theoretical analysis confirmed that for a metallic hyperbolical tip, the field emission current only increased sharply with the tip radius less than 25 nm [54]. However, our smallest NR diameter is about 86 nm, achieved with 0.17 at% of Y dopant concentration. Therefore, we expect that our NRs are too large to affect breakdown voltages and the discharge currents effectively.

Alternatively, the significant increase in discharge current accompanied with the reduction of breakdown voltages can be attributed to the increase in the conductivity of the Y-doped ZnO NRs. The correlation between the resistivity of NRs and the breakdown voltages, as well as the discharge currents for different gases can be clearly identified from Fig. 8. When the resistivity of the YZO decreased, the breakdown voltages were also reduced accordingly, while the reverse trend was observed for the discharge currents. At the minimum

resistivity, the minimum breakdown voltages and maximum discharge currents were achieved. Such behavior was observed for all tested gases. The increased conductivity of the NRs reduces the potential gradient across the NRs, which offers the increased effective electrical field strength at the apex of the NRs. The limited conductivity is a native drawback of metal oxide materials and the introduction of dopants helps to mitigate such problems. From the correlation analysis, it can be concluded that the resistivity of the NRs is a critical parameter for the performance of a GIS. For Si NRs GIS, metal encapsulation can also decrease the breakdown voltages significantly [55], which is in a good agreement with our conclusion. However, we would expect that the superior chemical and mechanical stability of conductive metal oxide could offer a more reliable GIS performance suitable for industrial applications.

#### **4. Conclusions**

We have demonstrated for the first time a stable and highly sensitive GIS device based on vertically aligned crystalline YZO NR arrays synthesized by a hydrothermal method. The surface morphology of the NRs was found to be strongly affected by the Y doping concentration. The increase in dopant concentration led to the formation of longer and sharper NRs with high aspect ratio. The introduction of Y into ZnO reduced the NR resistivity to its minimum by a factor of 115 for the  $Y_{0.10}ZO$ , which gave the highest sensitivity towards all the tested gas species with the lowest breakdown voltage.

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Figure Captions:

**Fig. 1.** A schematic diagram of NRs based GIS device.

**Fig. 2.** Top view SEM images of (A) ZnO NRs, (B)  $Y_{0.05}ZO$  NRs, (C)  $Y_{0.10}ZO$  NRs, (D)  $Y_{0.13}ZO$  NRs and (E)  $Y_{0.17}ZO$  NRs grown for 120 minutes. The insets show the magnified images. (F) Averaged diameter of the NRs as a function of Y concentration.

**Fig. 3.** Aspect ratio of YZO NRs as a function of Y doping concentrations.

**Fig. 4.** XRD patterns of ZnO and YZO NRs with various Y doping concentrations. The vertical dotted line indicates the  $2\theta$  position from (002) of pure ZnO.

**Fig. 5.** Electrical resistivity of YZO NRs as a function of Y concentration.

**Fig. 6.**  $I$ - $V$  curves for gas sensing characteristics of GISs based on ZnO NRs and YZO NRs with various Y doping concentrations in (A) air, (B)  $O_2$  (C)  $N_2$ , (D)  $CO_2$ , (E)  $CH_4$  and (F) Ar.

**Fig. 7.** (A) The stability tests of  $Y_{0.10}ZO$  NRs based GIS in air and  $N_2$  environments. Top view SEM images of  $Y_{0.10}ZO$  NRs (A) before and (B) after 100 cycles of continuous breakdown in  $N_2$  environment.

**Fig. 8.** (A) Breakdown voltages and (B) discharge currents of different gas species as a function of Y concentration. The dashed curve shows the resistivity of the YZO NRs as a function of Y concentration. Symbols represent different gas species: ( $\square$ )  $O_2$ , ( $\circ$ ) air, ( $\bullet$ ) Ar, ( $\times$ )  $CH_4$ , ( $\Delta$ )  $N_2$  and ( $\nabla$ )  $CO_2$ .